Comparative evaluation of biogas valorization into electricity/heat and polyhydroxyalkanoates in waste treatment plants: Assessing the influence of local commodity prices and current biotechnological limitations

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ABSTRACT

The transformation of CH_4-rich biogas into polyhydroxyalkanoates (PHA) using methanotrophic bacteria has recently emerged as an attractive and worldwide applicable alternative to its current use as energy source. The influence of the geographical location on the economic performance of combined heat and electricity production (CHP) and/or PHA production from biogas generated in waste treatment plants was evaluated in 13 representative regions of the world. In addition, the sensitivity of PHA production costs towards current biotechnological limitations and commodity prices was evaluated. The geographical analysis showed a high net present value (NPV_{20}) variability around the world (from -7.17 to +16.27 M€). Countries with the lowest NPV_{20} exhibited also the lowest PHA production costs (4.1 €·kg^{-1} PHA), which suggested that biopolymer production represents an alternative biogas valorization pathway in regions where CHP is not economically viable. In countries with high energy prices, the use of biogas surplus from anaerobic waste treatment for PHA production enhanced the economic performance and mitigated the electric market dependence of current CHP plants. CH_4-elimination capacity in bioreactors and PHA accumulation yield in bacterial cells were identified as the main biotechnological bottlenecks towards a biopolymer production competitive in price (0.2-1.7 €·kg^{-1} PHA) with their oil-based counterparts.

KEYWORDS

Biogas valorization; Biopolymers; Geographical analysis; Heat and Power Cogeneration (CHP); Methanotrophic bacteria; Polyhydroxyalkanoates (PHAs); Sensitivity analysis; Sustainability.

INTRODUCTION

The anaerobic digestion of organic waste (e.g. agricultural or municipal) was merely regarded as an effective method to reduce the amount of solid waste sent to landfill. The utilization of biogas as a renewable energy feedstock has boosted over the past decades the construction and operation of more than 25,000 large scale anaerobic digestion plants in the world, with an associated annual energy production of $3.5 \cdot 10^5$ GWh [1]. Fiscal incentives on renewable energy production from biogas (e.g. feed-in tariffs and carbon credits) have traditionally favored the installation of gas engines for electricity and heat co-generation (CHP) in certain regions of the world. Europe, and particularly Germany, has pioneered the construction of ~ 18,000 biogas plants, hosting two thirds of the global biogas electric capacity in 2017 [2].

Unfortunately, the current biogas production capacity only represents 2 % of the anaerobic digestion potential from currently available major feedstock (e.g. municipal solid waste, crop residues, animal residues, agro-industrial waste, wastewater, etc.), which could provide 16-22 % of the electricity consumed in the world while capturing 10-13 % of the global greenhouse gases emissions [3]. The uneven distribution of anaerobic digestion plants in the world can be attributed to the variability in commodity prices, the uncertainty in biogas price and the lack of policy drivers to develop sustainable alternatives to fossil fuels [4]. In addition, the high capital (400-1,100 €·kW^{-1}) and maintenance (0.01-0.02 €·kWh^{-1}) costs of gas engines, together with the rapid decrease in solar and wind energy prices (13 % cost reduction for solar and wind energies in the period 2017-2018), restrict the widespread implementation of electricity production from biogas worldwide [5, 6].

The unfavorable scenario for energy production from biogas, together with the urgent need for greener raw materials for the chemical industry, have recently attracted attention towards the

utilization of the methane (CH_4) contained in biogas as a precursor for the synthesis of bioproducts such as methanol, single cell protein or polyhydroxyalkanoates (PHA) [7]. PHAs constitute a family of biodegradable polymers with analogous characteristics to oil-based plastics and minimum environmental impacts [8]. They can be produced biologically from numerous solid and liquid carbon substrates (volatile fatty acids, glycerol, glucose, whey, etc). However, the inherent transportation and pretreatment costs, together with the acquisition costs of these raw materials, that account for up to 50 % of the total production costs, is still hindering its commercial mass production [9, 10]. In this context, biogas represents a locally produced feedstock with no additional transportation costs associated, with reduced pretreatment costs related to biogas desulfurization and with a decreasing value as renewable energy vector due to the steady decrease in the production costs of solar and wind power. Thus, the utilization of type II methanotrophic bacteria, capable of growing on CH_4-rich biogas for producing PHA under nutrient deprivation conditions, has emerged as a promising platform for decreasing PHA production costs and mitigating the misutilization of biogas in waste treatment plants [11]. However, the potential of CH_4-based bioproducts for promoting anaerobic digestion and the socio-economic context where biogas bioconversion into PHA will be able to compete with its current utilization for CHP in waste treatment plants remains unknown.

In this paper, a geographical analysis was performed evaluating the influence of fiscal incentives for renewable energy production and commodity prices (electricity, water and chemical reagents) on the economics of anaerobic digestion plants dedicated to CHP and/or PHA production from biogas in 13 representative cities of the world. Moreover, the sensitivity of PHA production costs towards current biotechnological limitations such as PHA bacterial accumulation yields, biomass concentration in the bioreactor and CH_4 biodegradation capacity, was studied.

MATERIALS AND METHODS

Model waste treatment plant

A medium-size municipal solid waste (MSW) treatment plant with a treatment capacity of 300 $t \cdot d^{-1}$ (750,000 person-equivalents) and a biogas production of 24,000 $Nm^3 \cdot d^{-1}$ was selected as model waste treatment plant. The size of the plant is considered representative for most of the MSW treatment plants that implement dry anaerobic digestion biogas valorization through CHP systems. Biogas thermodynamic properties (e.g. calorific power, Wobbe index) and concentrations of CH_4 (60 $\%v \cdot v^{-1}$), CO_2 (35 $\%v \cdot v^{-1}$), N_2 (2.5 $\%v \cdot v^{-1}$), O_2 (0.5 $\%v \cdot v^{-1}$), H_2S (0.4 $\%v \cdot v^{-1}$) and other minor compounds (1.6 $\%v \cdot v^{-1}$) were obtained from the Swedish Gas Technology Centre report [12]. Three biogas valorization scenarios were assessed in this analysis: (1) conventional desulfurized biogas combustion in CHP units for heat and electricity production, (2) desulfurized biogas bioconversion into PHA including extraction and purification of the biopolymer, and (3) a hybrid scenario where the necessary electricity and heat for PHA production and purification are provided by biogas combustion in CHP units (Figure 1).

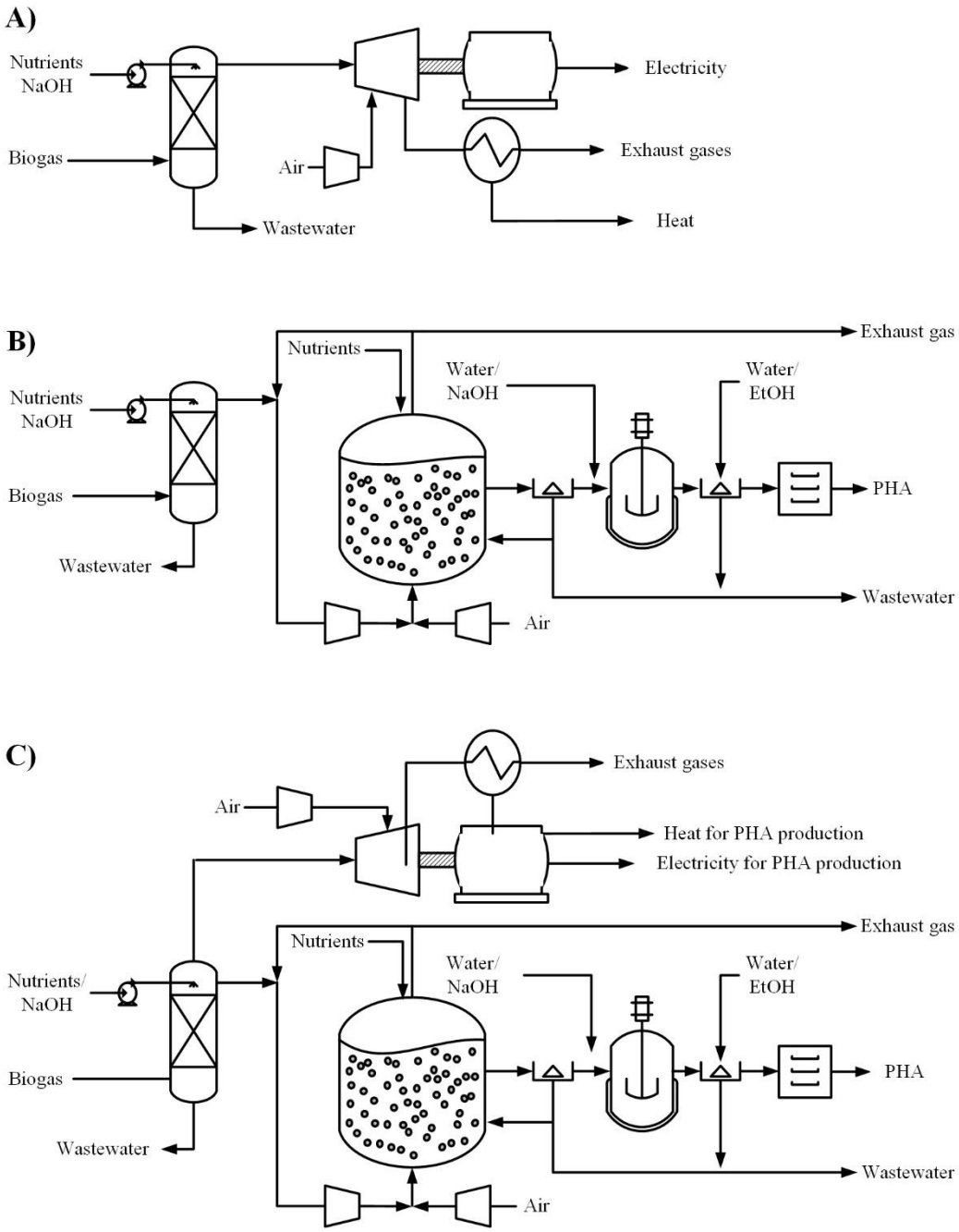

Figure 1. Process flow diagram for (A) desulfurized biogas combustion in CHP units, (B) bioconversion of CH_4 into PHA, and (C) a hybrid scenario where the electricity and heat required for CH_4 bioconversion into PHA are supplied by biogas combustion.

Process design

Biogas desulfurization

A biogas desulfurization stage for preventing the formation of H_2SO_4 in the presence of water and the associated corrosion of piping and equipment was considered in every scenario. Biological anoxic desulfurization was selected as model technology due to its low cost, reduced chemical requirements and high H_2S elimination performance (~99 % H_2S-removal efficiency (H_2S-RE)) [13]. This technology has been already successfully demonstrated at pilot scale in a real environment. Anoxic desulfurization relies on the action of sulfur oxidizing bacteria for oxidizing H_2S using nitrate (NO_3^-) instead of oxygen (O_2) as electron acceptor. A biotrickling filter packed with a mixture of inert materials and activated carbon with a pressure drop of 225 $Pa \cdot m^{-1}$ was designed at an empty bed residence time (EBRT) of 3 min and operated at ambient conditions of temperature and pressure (T = 15 ºC, P = 1.1 atm). A mineral salt medium (MSM) containing 50 g $NaNO_3 \cdot L^{-1}$ was supplied as trickling liquid at an average velocity of 10 $m \cdot h^{-1}$. A high N/S molar ratio (2.5) was applied for guaranteeing the selective oxidation of H_2S towards sulfate (SO_4^{-2}), thus avoiding elemental sulfur (S^0) accumulation in the packing medium. pH 7 was maintained via continuous addition of NaOH [14, 15].

Co-generation of heat and power

Gas engines are the most suitable and cost-effective technology for energy recovery from biogas in small and medium size facilities [5]. Gas engines for combined heat and power generation are based on the combustion of air/biogas mixtures for generating electricity (η_{el} = 40 %) while residual heat is recovered from the exhaust gases in the form of hot water or steam (η_{th} = 45 %). A lambda factor (λ) of 1.3 was selected, determining the excess of air required for biogas

combustion. Complete replacement of the gas engines was considered during the evaluated period (20 y) given the limited lifespan of gas engines (80,000 h) and a yearly utilization rate of 8,000 $h \cdot y^{-1}$. Approximately 40 % of the total electricity produced in the scenario of CHP production was devoted to internal energy provision in the pretreatment, sorting and anaerobic digestion process of the MSW in the three scenarios (personal communication for waste treatment operators). Medium-size waste treatment facilities rarely implement district heating systems for the surplus of heat produced given the distance to other plants capable of using the high volume of heat generated, and therefore was not considered in this study [16].

PHA biosynthesis, extraction and purification

PHA biosynthesis from biogas is based on the action of type II methanotrophic bacteria. These aerobic microorganisms are able to grow on CH_4-biogas as the sole carbon and energy source, and accumulate PHA as energy storage material in the absence of a nitrogen source [17]. The use of mixed methanotrophic cultures has been demonstrated as an effective strategy for PHA production, improving system robustness under long term operation and preventing culture contamination, avoiding the need of additional sterilization steps [18]. Biomass growth and biopolymer accumulation were considered to take place in a single bubble column bioreactor (BCB) equipped with internal gas recirculation. The recirculation of the outlet gas stream (×10 the influent gas flow rate) allows decoupling the EBRT (60 min) from the turbulence in the cultivation broth, thus achieving high CH_4-RE (90 %) in reduced reactor volumes [19]. A fine bubble diffusers grid with a pressure drop of 7 kPa was installed at the bottom of the bioreactor for supplying the optimum air/biogas mixture for CH_4 aerobic biodegradation (O_2:CH_4 = 1.5 $mol \cdot mol^{-1}$). The BCB was operated at ambient conditions of temperature and pressure (T = 15 ºC; P = 1.1 atm).

The operation followed a fed-batch strategy alternating feast-famine cycles of 30 g $NaNO_3 \cdot L^{-1}$ MSM (growth phase) and water (accumulation phase). Biomass growth (0.67 g biomass$\cdot g^{-1}$ CH_4) and PHA accumulation (0.55 g PHA$\cdot g^{-1}$ CH_4) were considered according to the corresponding stoichiometry (Table S1). Only 7.5 % of the PHA accumulated in methanotrophic bacteria was consumed during the growth phase in the presence of nitrogen [19].

Alkaline treatment with NaOH was selected for PHA extraction given its cost-effectiveness and the high recovery (80 %) and purity (92 %) of the biopolymer obtained [20]. In this context, the cultivation broth from the bioreactor is initially centrifuged and the excess liquid is recycled to the bioreactor to harness the residual amount of nutrients and biomass. The concentrated methanotrophic sludge (2.5 % w$\cdot w^{-1}$) is treated with NaOH (0.8 g NaOH$\cdot g^{-1}$ biomass) in a continuous stirred tank reactor equipped with an external jacket with circulating water as thermal fluid for 5 h at 37 ºC [20]. Complete biomass solubilization and negligible PHA degradation during the extraction process were assumed. Product purity and recovery deviations from 100 % during the extraction process were attributed to the difficult separation of liquid and solid phases [20]. Subsequently, the biopolymer was concentrated by centrifugation and double washed with water and ethanol in order to remove impurities. Finally, the product was dried in a tray filter with warm air at 60 ºC to a final moisture of 2 %. Main process equipment dimensions and process design parameters are described in Table S2.

Capital and operational costs

Total capital investment costs (TIC) were estimated from the individual process equipment cost (PEC) according to the Lang's method. In particular, a Lang multiplier of 4.1 was selected as recommended by Ulrich and Vasudevan for solid-liquid processes [21]. This factor already considers

all the control systems, direct costs, electrical installations and safety related equipment. In addition, the process incorporates inherent safety measures by operating with CH_4-air mixtures below the biogas explosion limits < 5 %v/v of CH_4. Average equipment prices based on quotations from Spanish and international companies, literature reviews and online estimation tools were used in order to compensate the geographical influence on equipment costs, given the difficulties finding reliable price sources in all the regions studied and the inherent cost uncertainties of preliminary techno-economic studies like the one presented in this article. It should be mentioned that high-quality materials were considered in this study to avoid the corrosion caused by H_2S during the biogas desulfurization in a biotrickling filter and by NaOH during PHA purification and extraction. PEC for pumps, compressors, centrifuges and bioreactors was calculated by comparison of quotations with international companies, literature review and online estimation tools [22, 23]. In the case of gas engines and BCBs, Lang's method was not applied as the prices already considered fabrication and installation of the equipment. For CHP gas engines, capital costs (including commissioning and installation) of 1000 €·kW^{-1} and operational costs (including operation and maintenance) of 0.015 €·$kWhel^{-1}$ were assumed [5]. The use of concrete as construction material for the BCBs was considered due to its low-cost (190 €·m^{-3} including civil work and construction) compared to traditional materials such as stainless steel that would result in economically unsustainable prices (2,500 €·m^{-3}).

Operational costs including water, energy, steam and raw materials were calculated according to mass balances. Costs of goods and services include costs indirectly related to process operation namely insurances, laboratory analysis, research and innovation expenditure, quality control tests, potential certifications required and the cost of stocking raw materials and products. These costs were estimated as 20 % of the total energy, water and raw materials costs. Additional costs for

solid waste and wastewater treatment were considered negligible due to their low volumetric flows and organic loads when compared to typical flows and composition of the digestate originated in medium size waste treatment plants. Water and electricity costs were obtained from national suppliers (Table 1). The cost of chemical reagents was gathered from quotations with international companies. Steam requirements for the anaerobic digestion process were estimated at 0.08 kg steam·kg^{-1} waste with a price of 0.014 €·kg^{-1}. Power consumption of pumps and compressors was calculated according to Equation 1, where P stands for the power consumption in kW, Q is the volumetric flow in m^3·s^{-1}, ΔP indicates the pressure drop in kPa and η is the pump and compressor efficiency (70 %) [24].

$$P = \frac{Q \cdot \Delta P}{\eta} \qquad (1)$$

Geographical analysis

The economic performance of anaerobic digestion plants dedicated to CHP and/or PHA production was evaluated in 13 representative cities in the absence and presence of fiscal incentives on renewable energy production. The cities were selected in order to assess the high variability of commodity prices (water, electricity and chemical reagents) and of levels of adoption of anaerobic digestion technologies in the different regions of the world: (sorted by increasing order of energy price) Doha (Qatar, Middle East), Johannesburg (South Africa, African emerging countries), New Delhi (India, Asian emerging countries), Shanghai (China), Toronto (Canada, North America East Coast), Sofia (Bulgaria, Eastern Europe), Copenhagen (Denmark, Central and Northern Europe), Madrid (Spain, Southern Europe), Los Angeles (USA, North America West Coast), Singapore

(Singapore, Asia), Sao Paulo (Brazil, South America), Tokyo (Japan, Asia), Sydney (Australia, Asia-Pacific) [25].

Industrial water and energy purchase prices were compiled from national suppliers (Table S3 and Table S4). The energy selling price was estimated as 70 % of the energy purchase price due to the difficulties in finding reliable literature sources for national regulations on energy production. The difference between energy purchase and selling prices accounts for the production and distribution taxes on energy production. In the scenario of fiscal incentives for renewable energy production, energy selling prices were considered equal to energy purchase prices, which is considered the best-case scenario for industrial energy producers [26]. The cost of chemical reagents was adjusted according to the price level calculated with Equation (2), where CLI_i stands for the Cost of Living Index in each region, using Madrid (Spain) as a reference city [27].

$$\text{Price Level} = \frac{\text{CLI}_\text{i}}{\text{CLI}_\text{Madrid}} \quad (2)$$

Table 1. Summary of electricity and water prices compiled from national suppliers.

Reference cities	Electricity price (€·kWh^{-1})	Water price (€·m^{-3})	Price level
Doha (Qatar)	0.020	1.21	1.06
Johannesburg (South Africa)	0.070	1.95	0.76
New Delhi (India)	0.070	0.58	0.47
Shanghai (China)	0.072	0.19	0.84
Toronto (Canada)	0.076	2.28	1.40
Sofia (Bulgaria)	0.083	1.00	0.69
Copenhagen (Denmark)	0.083	5.59	1.48
Madrid (Spain)	0.104	1.89	1.00
Los Angeles (USA)	0.117	2.70	1.31
Singapore (Singapore)	0.157	0.43	1.38
Sao Paulo (Brazil)	0.159	2.13	0.77
Tokyo (Japan)	0.166	1.90	1.49
Sydney (Australia)	0.215	1.27	1.35

The net present value for a 20-years horizon (NPV_{20}), the internal rate of return (IRR) and the payback period (PP) were considered as economic performance indicators in this comparative assessment. NPV_{20} was calculated using Equation 3, where TIC stands for the total investment cost at year 0, t indicates the accounting year, Ft is the free cash flow at year t and r represents the interest rate [25]. A linear depreciation over the first 10 years, a tax rate of 30 % and an interest rate

of 5 % were considered for NPV_{20} calculations. IRR was calculated as the value of the interest rate at NPV_{20} equal to zero and PP was determined as the first period at which NPV_{20} becomes positive.

$$NPV_{20} = TIC - \sum_{t=1}^{t=20} \frac{F_t}{(1+r)^t} \quad (3)$$

PHA production costs were calculated as the break-even price at which NPV_{20} becomes positive for each scenario. For this geographical analysis a CH_4 elimination capacity (CH_4-EC) of 60 $g \cdot m^{-3} \cdot h^{-1}$, biomass concentration (X) of 30 $g \cdot L^{-1}$ and PHA accumulation capacity of 40 % ($w \cdot w^{-1}$) were selected [17, 19, 28].

Sensitivity analysis

A sensitivity analysis on PHA production costs was performed for the cities showing the highest (Sidney (Australia)) and lowest (Doha (Qatar)) NPV_{20} on CHP from biogas. CH_4 and O_2 supply from the gas phase to the cultivation broth, biomass cell density in the bioreactor and PHA bacterial accumulation capacity have been identified in literature as the major factors affecting PHA production costs and reducing its market competitiveness [29]. This sensitivity analysis aimed at evaluating the decrease in PHA production costs derived from future biotechnological advances (represented by the optimum values of these parameters, Table 2), thus defining the roadmap to develop cost-competitive biogas biorefineries.

High O_2 mass transfer rates of 500 g $O_2 \cdot m^{-3} \cdot h^{-1}$ were reported by Fernandez-Dacosta and co-workers during the production of PHA from wastewater in a similar bioreactor [30]. This value would correspond to a CH_4-EC of 428 g $CH_4 \cdot m^{-3} \cdot h^{-1}$ according to the equation proposed by Yu et al. ($k_La O_2 = 1.169 \cdot k_La CH_4$), given the comparable liquid solubility of CH_4 and O_2 [31]. A maximum

biomass concentration of 100 $g \cdot L^{-1}$ was selected, which is in line with the values previously reported for PHA production from glucose with *Methylobacterium organophilum* (250 $g \cdot L^{-1}$) and recombinant *Escherichia coli* (113 $g \cdot L^{-1}$) [29, 32]. A maximum PHA accumulation capacity of 90 % ($w \cdot w^{-1}$) was considered based on the PHA content of *Cupriavidus necator* (87 % $w \cdot w^{-1}$) in a continuous bioreactor as described by Hafuka and co-workers [33]. Similarly, Aljuraifani et al. reported PHA accumulation capacities >90% in *Pseudomonas* strains using waste carbon streams such as rice bran, dates and soy molasses [34].

Table 2. Summary of process performance parameters considered for the sensitivity analysis on PHA production costs.

Parameter	Values
Minimum CH_4-EC ($g \cdot m^{-3} \cdot h^{-1}$)	60 [19]
Maximum CH_4-EC ($g \cdot m^{-3} \cdot h^{-1}$)	428 [30]
Minimum X ($g \cdot L^{-1}$)	30 [28]
Maximum X ($g \cdot L^{-1}$)	100 [29]
Minimum PHA accumulation (% $w \cdot w^{-1}$)	40 [17]
Maximum PHA accumulation (% $w \cdot w^{-1}$)	90 [33, 34]

RESULTS AND DISCUSSION

Geographical analysis

The influence of electricity, water and chemical reagents prices on the economic performance of biogas valorization into CHP and/or PHA was evaluated in 13 representative cities of the world. The TIC for the production of CHP, PHA and the combined scenario was estimated at 6.0, 7.7 and

8.1 M€, respectively (Table S5). For CHP production, the commissioning of gas engines was identified as the main cost (4.9 M€), while the construction of BCBs and the installation of multiple air/biogas compressors for CH_4 biodegradation resulted in the most significant equipment costs in PHA production (1.2 M€ and 4.4 M€, respectively). In the hybrid scenario, 32 % of the biogas stream was used as substrate for methanotrophic PHA-accumulating bacteria, while the remaining 68 % was dedicated to the production of energy and heat to cover the energy requirements of the MSW processing (40 %) and biogas bioconversion into PHA followed by biopolymer extraction (28 %). A TIC of 3.4 M€ for the CHP engines and 3.3 M€ for the production of PHA (mainly dedicated to the acquisition of BCBs, pumps and compressors) were calculated in this scenario.

The operational costs of CHP ranged from 318,537 $€\cdot y^{-1}$ in New Delhi to 495,024 $€\cdot y^{-1}$ in Copenhagen, as a result of the higher prices of water (0.58 and 5.59 $€\cdot m^{-3}$, respectively) and chemical reagents (price level of 0.47 and 1.48 for New Delhi and Copenhagen compared to Madrid, respectively) required for the preliminary biogas desulfurization step (Figure 2A). In contrast, sales revenue (including sales of energy to the electric market and savings derived from energy and heat self-production) were minimum in Doha with 275,743 $€\cdot y^{-1}$ and maximum in Sydney with 3,002,852 $€\cdot y^{-1}$, due to the significant differences in energy prices (0.02 and 0.21 $€\cdot kWh^{-1}$ in Doha and Sydney, respectively) (Figure 2A).

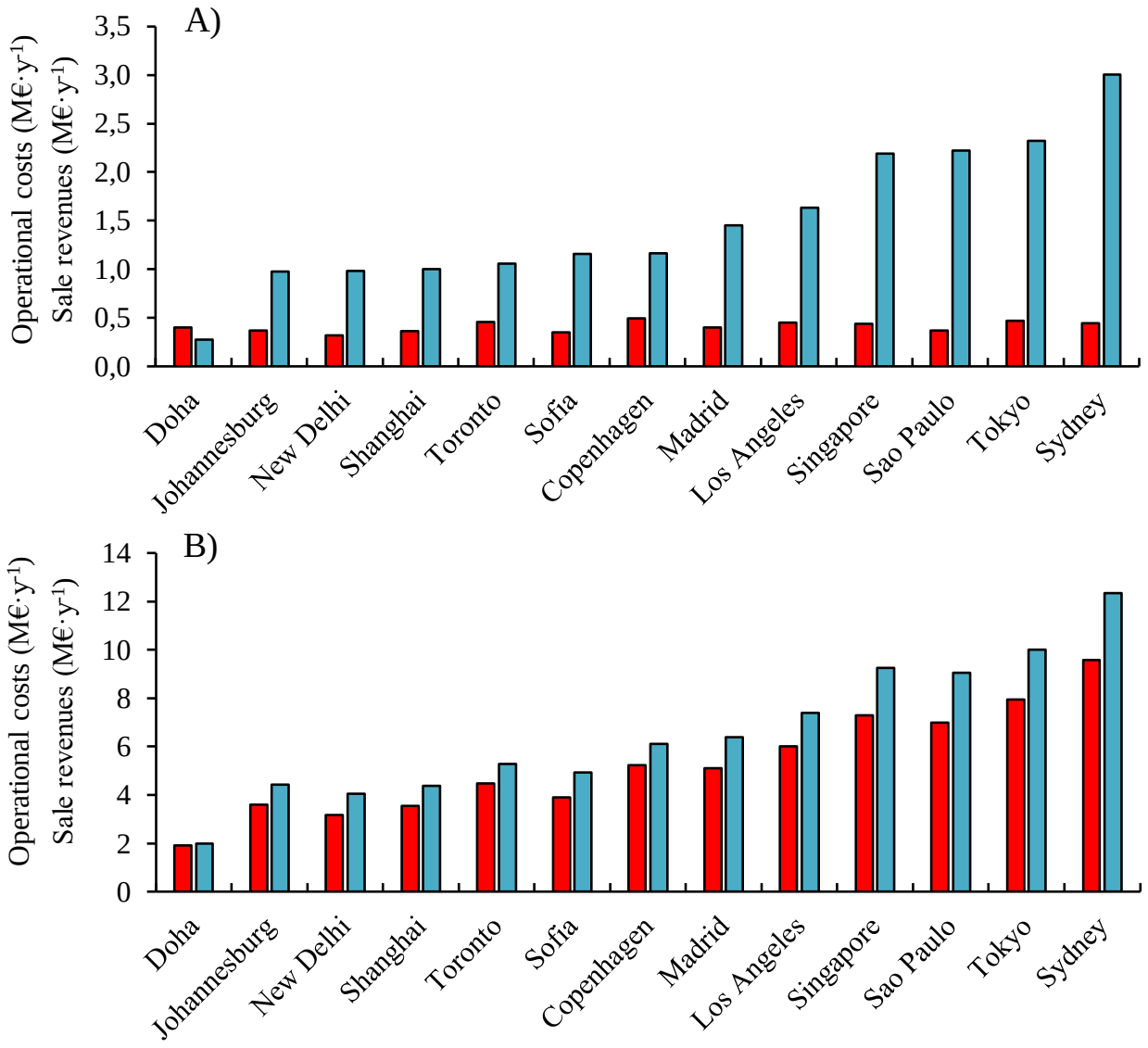

Figure 2. Influence of the geographical location of the plant evaluated in 13 regions of the world on the operational costs (■), and sales revenue (■) for (A) biogas valorization into heat and electricity with CHP engines and (B) biogas valorization into PHA. Cities are sorted in increasing order of energy cost.

The geographical evaluation of NPV_{20} for biogas valorization using CHP in the absence of fiscal incentives showed a high variability (from -7.17 to +16.27 M€ in Doha and Sydney, respectively),

correlated with the disparity in energy prices (Figure 3). The IRR and the PP were calculated altogether with the NPV_{20} to assess the risk of investment on CHP (Figure 4). Different authors have previously discussed the critical PP for CHP profitability, with reported values ranging from less than 7 up to 12 years [35, 36]. At this point it should be stressed that the PP and IRR in Doha could not be calculated based on the negative NPV_{20} previously estimated.

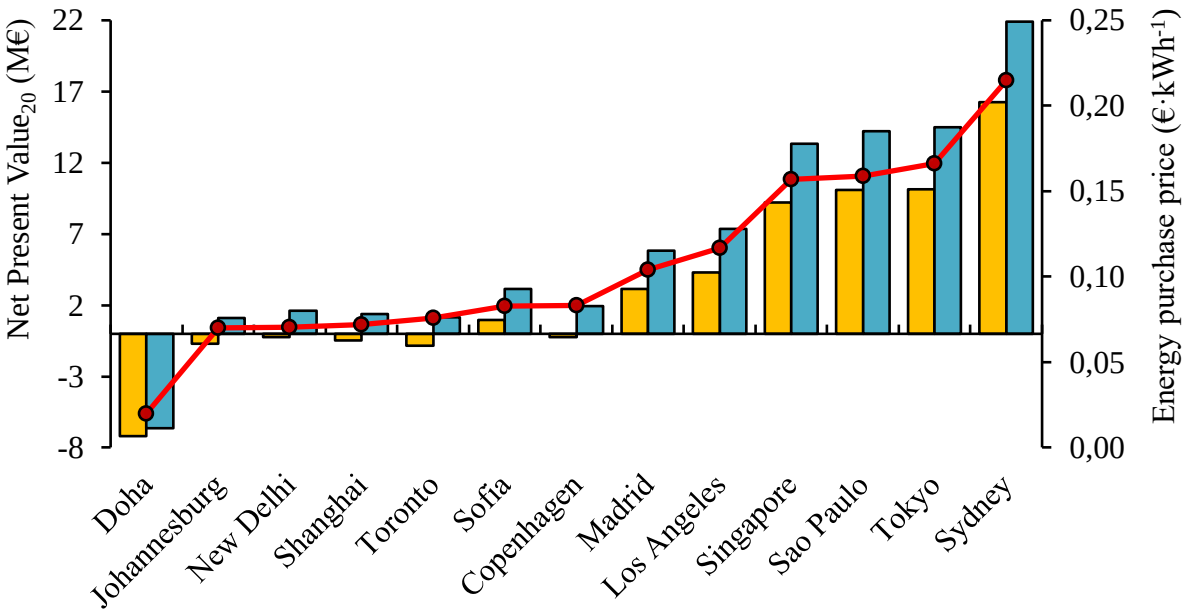

Figure 3. Influence of the geographical location of the plant on the NPV_{20} evaluated in 13 representative cities of the world in the absence (▭) and presence (▭) of fiscal incentives on renewable energy production. Continuous red line represents the energy purchase price in each country.

In this study, Singapore, Sao Paulo, Tokyo and Sydney were the only regions showing rapid payback times below 7 years, while the investment in Madrid and Los Angeles could be recovered in less than 12 years. Given the reduced margin between operational costs and sales revenue, the

investment on CHP engines was demonstrated as unprofitable in scenarios where energy purchase prices are below 0.083 €·kWh^{-1} (Copenhagen). The implementation of tax incentives on renewable energy production improved the revenue from sales by 21 % in all the regions studied, with a great impact on the overall economic feasibility. This result was especially relevant for countries like South Africa, India, China, Canada or Denmark, where a positive or negative NPV_{20} depended on the application of these fiscal incentives. Additionally, the expected decrease in energy prices due to the increase of renewable energy share in the energy pool (35 and 19 % global increase in solar and wind electric power generation, respectively, compared to 2016) and the decrease in their generation costs (13 % reduction in 2018 for solar and wind energy prices compared to 2017) jeopardize the profitability of future CHP investments in cities with moderate energy prices such as Madrid (0.10 €·kWh^{-1}) or Los Angeles (0.12 €·kWh^{-1}) [6].

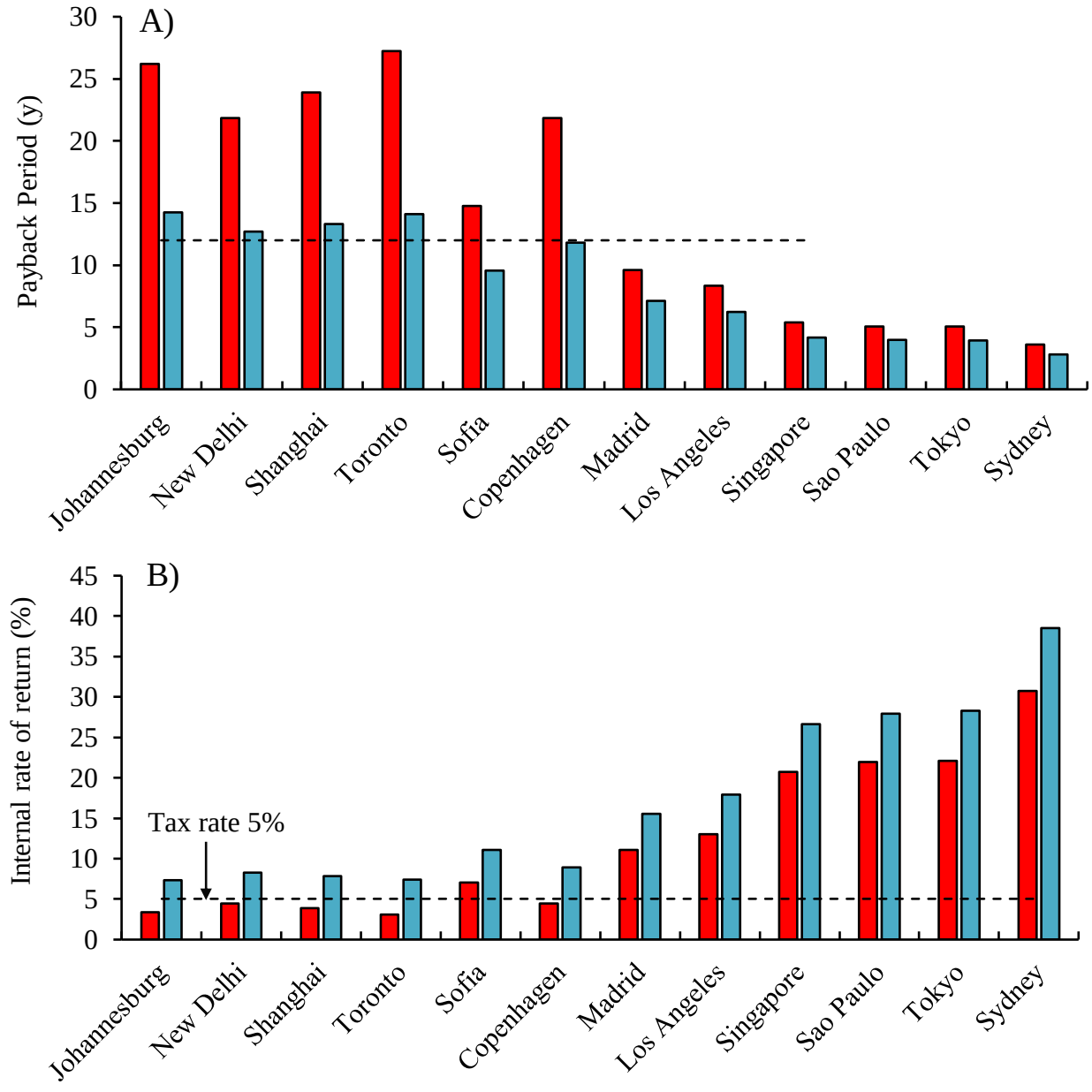

Figure 4. Influence of the geographical location evaluated in 13 representative cities of the world on (A) the payback period and (B) the internal rate of return in the absence of fiscal incentives (■) and with fiscal incentives on renewable energy production (■). Dashed line represents in (A) the maximum payback period recommended for accepting CHP investments, and (B) the current tax rate.

This foreseen unfavorable scenario for energy production from biogas has emerged as an opportunity for promoting alternative biogas valorization platforms in waste treatment plants, such as CH_4-biogas bioconversion into PHA. In this geographical analysis, the influence of commodity (water, energy and chemical reagents) prices on PHA production costs was evaluated. When biogas was allocated exclusively to biopolymer production, PHA production costs ranged from 4.1 €·kg^{-1} in Doha to 15.4 €·kg^{-1} in Sydney (Figure 5A). These values lied within the typical range estimated for PHA production from different carbon substrates and bacterial strains (4-20 €·kg^{-1}) [9]. Likewise, they agreed with those first reported for the biosynthesis of poly(3-hydroxybutyrate) (PHB) from natural gas using methanotrophic bacteria (11.5-14.0 €·kg^{-1}) [37]. Energy consumption was identified as the main cost share for PHA production in all regions of the world (excepting Doha), followed by the cost of goods and services and chemical reagent costs. The individual cost shares varied greatly depending on the region of the world, ranging from 32.3 to 71.4 %, 0.5 to 10.6 % and 8.9 to 44.8 % for energy, water and raw materials, respectively. Heat requirements for the extraction process were lower than electricity consumption in all scenarios evaluated, representing < 2 % of the total energy required. Contrarily to CHP, countries with lower energy prices are the best candidates to cost-effectively produce PHA from biogas. Indeed, Doha was the only region showing PHA production costs (4.1 €·kg^{-1}) comparable with the current PHB selling price estimated by Stanford University (4.7 \$·kg^{-1}; 4.3 €·kg^{-1}) [38]. This can be viewed as an opportunity for developing anaerobic digestion plants in regions of the world where CHP production has not been (or will soon not be) economically sustainable. Alternatively, when heat and electricity were self-provided by CHP engines using the *in-situ* produced biogas, PHA production costs decreased drastically at the expense of a reduction in PHA production capacity from 681 to 216 ton·y^{-1}. When energy costs were minimized by the implementation of CHP gas

engines on-site, PHA production costs concomitantly decreased to prices ranging from 6.9 to 1.5 €·kg^{-1} in Doha and Sydney, respectively, below the median price found in literature for all sort of carbon raw materials (7.5 $·kg^{-1}; 6.8 €·kg^{-1}) [39]. In addition, it was demonstrated that the combination of CHP generation with PHA synthesis allows the production of commercially viable biopolymers (3-5 €·kg^{-1} according to Calrecycle Report) in countries with high energy prices [38]. Interestingly, recent studies indicated that energy production (electricity and heat) and transportation of raw materials were responsible for most of the ecological footprint of PHA production from waste streams (e.g. animal residues and whey) [40,41]. Particularly, these literature studies showed the high dependence of the environmental impacts on the local energy mix used for electricity and heat provision. Thus, the use of locally produced biogas as both renewable energy vector and carbon source for PHA production would reduce drastically the ecological pressure of biopolymer production. These results demonstrated that biogas represents a globally available and sustainable feedstock for producing low-cost PHA and that using biogas surplus (after satisfying energy demand for MSW processing) for producing PHA instead of energy constitutes an alternative for enhancing the economic performance and reducing the environmental impact and the electric market dependence of current CHP plants.

In recent years, PHA production from volatile fatty acids (VFAs) and from biogas using methanotrophic bacteria have gained increasing attention [17, 42, 43]. Up to now, the two options have demonstrated promising results at laboratory scale. The use of VFAs for the production of PHA entails some additional challenges like the high variability of VFAs composition, in contrast to the more predictable composition of biogas, which could affect biopolymer composition and quality. In addition, PHA production from VFA at full scale requires the implementation of two-stage anaerobic digestion processes, separating the acidogenic and methanogenic phases, while PHA

production from biogas do not require of any significant modification in the current biological organic waste treatment process [43]. Finally, PHA production from biogas could benefit from the addition of small quantities of VFA, which modifies biopolymer properties [17].

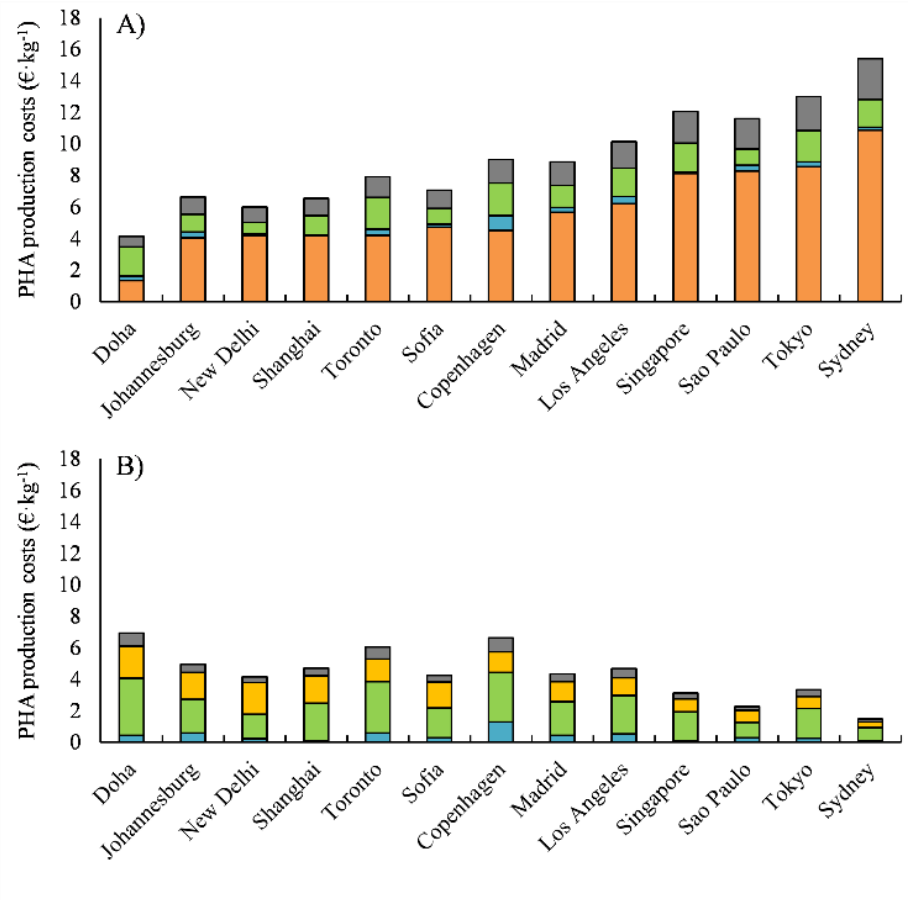

Figure 5. Influence of the geographical location evaluated in 13 representative cities of the world on PHA production costs in plants dedicated to (A) PHA production from biogas, and (B) combined CHP generation and PHA production. Cumulative bars represent the cost of: (■) electricity, (■) water, (■) raw materials, (■) CHP production and (■) other costs.

Sensitivity analysis

The sensitivity of PHA production costs towards current biotechnological limitations such as CH_4 biodegradation capacity, PHA bacterial accumulation yields and biomass concentration in the

bioreactor was evaluated. The sensitivity analysis was focused on the cities showing the lowest (Doha) and highest (Sydney) NPV_{20} on CHP from biogas. In addition, these cities presented the lowest PHA production costs for biopolymer production from biogas (Doha; 4.1 €·kg^{-1}) and for simultaneous CHP and PHA production (Sydney; 1.5 €·kg^{-1}).

First, the effect of the aforementioned factors was assessed individually in order to identify their separate contribution to PHA production costs. An increase in the CH_4 elimination capacity from 60 to 428 g CH_4 m^{-3} h^{-1} exerted a great impact on PHA production costs. Indeed, PHA production costs decreased from 4.1 to 3.4 €·kg^{-1} in Doha and from 1.5 to 0.4 €·kg^{-1} in Sydney. Comparable PHA prices (1.5–2 €·kg^{-1}) were reported by Fernández-Dacosta and co-workers during the production of PHA from wastewater assuming the same oxygen mass transfer rate (500 g O_2·m^{-3}·h^{-1}) and a higher PHA accumulation (70 %w·w^{-1}) [30]. In addition, the results herein obtained were in well agreement with those reported by Choi and co-workers during the co-production of hydrogen and PHA from syngas fermentation (1.5 €·kg^{-1}) and Shahzad and co-workers during the co-production of biodiesel, meat-bone-meal and PHA using slaughtering waste streams (1.41 – 1.64 €·kg^{-1}) [10, 44]. This increase in CH_4 gas-liquid mass transfer was associated to a significant decrease in process TIC (from 7.7 and 8.1 M€ to 3.5 and 5.9 M€, for PHA production and simultaneous CHP and PHA production, respectively) as a result of the reduction of the total reaction volume. This reaction volume reduction results in a lower amount of bioreactors and the number of associated equipment required for methanotrophic bacteria cultivation.

On the other hand, the increase in bacterial PHA accumulation from 0.4 to 0.9 w·w^{-1} resulted in an enhanced biopolymer production capacity as the carbon contained in CH_4-rich biogas was preferentially transformed into PHA instead of being used for biomass growth. Thus, PHA annual production doubled from 681 to 1406 ton·y^{-1} when biogas was exclusively used for biopolymer

production and from 216 to 447 ton·y^{-1} in the CHP and PHA combined scenario. This increase in PHA productivity resulted in PHA production costs of 1.9 and 0.6 €·kg^{-1} in Doha and Sydney, respectively.

Finally, the increase in biomass concentration in the culture broth mediated a marginal effect on PHA production costs, from 4.1 to 4.0 €·kg^{-1} and from 1.5 to 1.4 €·kg^{-1} in Doha and Sydney, respectively. These cost reductions were attributed to the marginal contribution in energy consumption during biomass centrifugation and biopolymer separation processes to the total energy costs, which represents 3.8 % and 2.8 % of the total energy consumed in the scenario of 30 g·L^{-1} and 100 g ·L^{-1}, respectively. This mild decrease in cost can be explained by the fact that biological reaction kinetics are limited by CH_4 gas-liquid mass transfer and the annual PHA production is constrained by the amount of biogas produced from waste. Therefore, the increase in biomass concentration in the bioreactor results in an increase of the reaction time in the biogas fermenter but PHA productivity remains invariable.

Interestingly, none of the target factors exerted a significant influence on the operational costs of PHA, but mediated different effects on the investment costs and on PHA productivity. In view of the results, biomass concentration was maintained at 30 g·L^{-1} and the combined effect of increasing CH_4 elimination capacity and PHA accumulation was investigated for both scenarios. All combinations of CH_4-EC and PHA accumulation were assessed and the results are depicted in Figure 6.

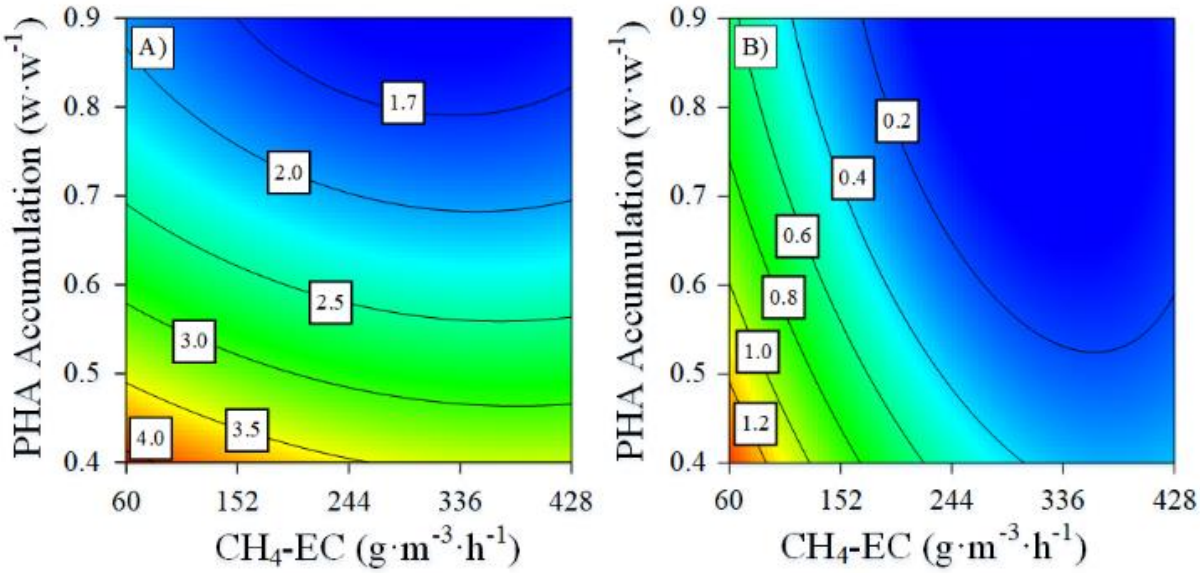

Figure 6. Influence of PHA accumulation yield and CH4-EC on PHA production costs (€·kg^{-1}) at X = 30 g·L^{-1} for (A) a plant located in Doha (Qatar) dedicated exclusively to PHA production from biogas and (B) a plant located in Sydney (Australia) combining CHP and PHA production from biogas.

The size of the contour plots in Figure 6 suggests that despite both factors were relevant to decrease the production costs down to 1.6 €·kg^{-1} when biogas was entirely devoted to biopolymer production, PHA accumulation yield (and therefore PHA productivity) was dominant. In contrast, the reduction of TIC caused by the increase in CH_4 elimination capacity in plants combining CHP and PHA was more relevant to the final biopolymer price (down to 0.2 €·kg^{-1}). These low PHA selling prices associated to future biotechnological advances are well below to the forecasted market price for PHA bacterial biopolymers in 2035 (2.0–1.7 €·kg^{-1}) [38]. Overall, this study showed that there exists a global opportunity for producing PHA from biogas in waste treatment plants at prices competitive with their oil-based counterparts. Different strategies, such as improving CH_4 biodegradation in bioreactors and selecting high-PHA accumulating strains, can be followed

depending on the region of the world in order to maximize benefits and decrease PHA production costs.

CONCLUSIONS

In summary, this study demonstrated that biogas constitutes a worldwide available and suitable feedstock for PHA production in waste treatment plants. The geographical analysis indicated that the economic performance of anaerobic digestion plants dedicated to CHP production exhibited a strong dependence on local commodity prices. Particularly, the variability in electricity acquisition costs determined the economic feasibility of biogas transformation into heat and electricity, with NPV_{20} values ranging from -7.17 to +16.27 M€. The geographical analysis also demonstrated that the production costs of biogas-based PHA were comparable to the production costs of PHA from other waste carbon substrates. The regions with the lowest electricity prices also exhibited the lowest PHA production costs (4.1 €·kg^{-1}), raising as an opportunity for the widespread implementation of anaerobic digestion in these regions. In contrast, the combination of CHP generation and PHA production from biogas in countries with high energy prices is recommended for producing cost-competitive PHA (1.5 €·kg^{-1}). Finally, the sensitivity analysis showed a significant impact of CH_4-EC and PHA accumulation yield on process TIC and PHA annual production. Overcoming these biotechnological limitations will allow reducing PHA production costs down to 0.2-1.9 €·kg^{-1}, which would render them competitive in price with their oil-based counterparts.

SUPPORTING INFORMATION

Table S1. Stoichiometry of methanotrophic bacteria growth and PHA accumulation using CH4 as the only carbon source.

Table S2. Summary of process design parameters and equipment dimensions.

Table S3. Compilation of literature sources for selection of energy purchase prices in each region studied.

Table S4. Compilation of literature sources for selection of industrial water purchase prices in each region studied.

Table S5. Summary of purchased equipment cost and total investment cost.

Figure S1. Global mass and energy balance of biogas valorization into CHP. In blue, mass flows in kg/d. In red, energy flows in $kWh \cdot d^{-1}$.

Figure S2. Global mass and energy balance of biogas valorization into PHA. In blue, mass flows in kg/d. In red, energy flows in $kWh \cdot d^{-1}$.

Figure S3. Global mass and energy balance of combined biogas valorization into CHP and PHA. In blue, mass flows in kg/d. In red, energy flows in $kWh \cdot d^{-1}$.

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ABBREVIATIONS

BCB, Bubble Column Bioreactor

CHP, Combined Heat and Power

CLI, Cost of Living Index

EBRT, Empty Bed Residence Time

EC, Elimination Capacity

IRR, Internal Rate of Return

MSM, Mineral Salt Medium

MSW, Municipal Solid Waste

NPV_{20}, Net Present Value

PEC, Purchased Equipment Cost

PHA, Polyhydroxyalkanoate

PHB, Poly(3-hydroxybutyrate)

PP, Payback Period

RE, Removal Efficiency

TIC, Total Investment Cost.

VFA, Volatile Fatty Acid

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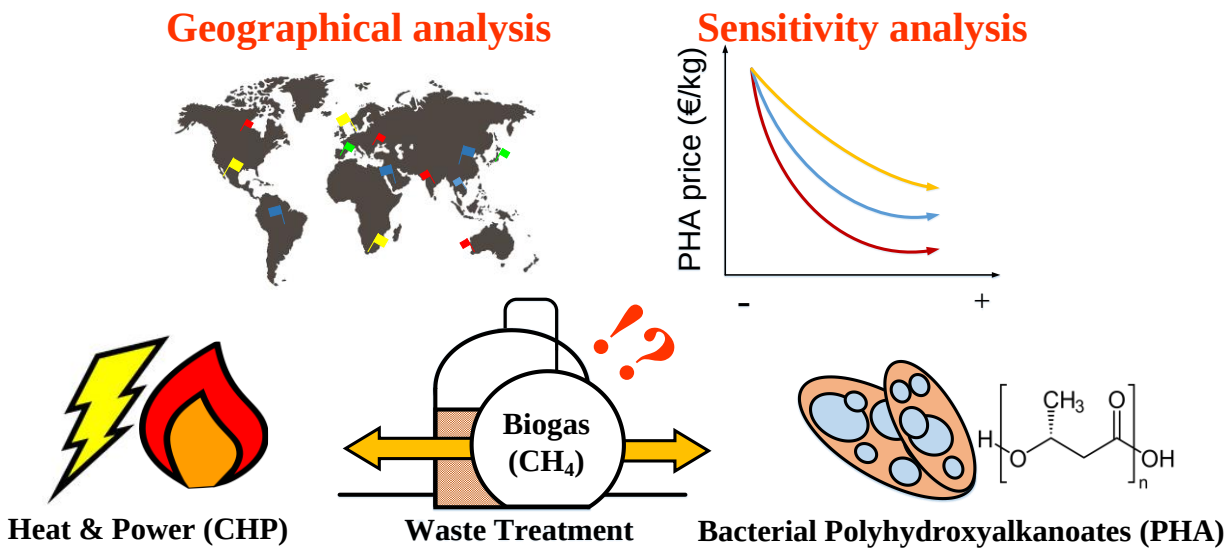

SYNOPSIS: A geographical and sensitivity comparative assessment between two biogas valorization alternatives: heat and electricity co-production and bioconversion into polyhydroxyalkanoates (PHA).